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(54) Improved machine dishwashing and rinsing composition.

(57) Machine dishwashing and rinsing compositions are provided having improved foam control properties by inclusion of an effective amount of a special group of polymers, which consists of polyelectrolytes containing cationic charges and having a cationic charge to carbon atom in the backbone ratio of from 0.03 to 0.5 and a molecular weight in the range of from $5 \cdot 10^3$ to $5 \cdot 10^5$. A typical example of such a polyelectrolyte is the copolymer of N-vinylpyrrolidone and quaternized diethylaminoethylmethacrylate.

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IMPROVED MACHINE DISHWASHING AND RINSING COMPOSITION

The present invention relates to an improvement in machine dishwashing and rinsing compositions.

In machine dishwashing processes usually two products are applied, i.e. a machine dishwashing composition for use in the main wash cycle, and a rinse aid composition for use in the rinse cycle. Both products usually contain an active detergent material. Since both products are applied to the articles to be cleaned or rinsed by spraying the wash or rinse liquor containing these products thereon, which implies the use of a pump, the generation of too much foam thereby is a serious problem. Too much foam can cause too much noise, may damage the heating coil of the dishwashing machine, can lead to the pump malfunctioning and may impair the overall efficacy of the dishwashing process. Consequently, only low-foaming active detergent materials are commonly used in machine dishwashing and rinsing compositions.

Nevertheless, still too much foam can be generated, e.g. by the soil removed from the articles to be cleaned, if no additional measures, such as the use of foam depressing agents are taken. This foam formation can cause the pressure of the pump with which the wash liquor or the rinse water is sprayed upon the articles to be cleaned to drop, which produces the above-mentioned disadvantages.

It is therefore an object of the present invention to provide for a machine dishwashing or rinse composition which, when in use in a dishwashing or rinsing operation, prevents the pump pressure from dropping to any significant degree.

It has now been found that this object can be achieved by the inclusion in a machine dishwashing or rinsing

composition of a small, effective amount of a special group of polymers. The machine dishwashing or rinsing composition, in which the special group of polymers is included, is of the usual type and formulation,

- 5 containing as active detergent material a nonionic detergent, preferably a low-foaming one.

In its broadest aspect therefore, the invention relates to a machine dishwashing or rinsing composition 10 comprising a nonionic detergent, and is characterized by the inclusion therein of a small, effective amount of a special group of polymers.

The special group of polymers consists of polyelectrolytes which contain cationic charges, either permanent or at the pH of usage. They have a cationic charge to carbon atom in the backbone ratio of from 0.03 to 0.5. They may contain additional neutral or anionic groups, with an anionic to cationic group ratio of as high as 3 : 1. They 20 have a molecular weight in the range of $5 \cdot 10^3$ to $5 \cdot 10^5$.

The special group of polymers consists of three kinds of polymers, i.e. those based on quaternized diethylamino-25 ethylmethacrylate, those based on dimethyldialkylammoniumhalide, and quaternized polysaccharides.

To the first class belongs as typical example a copolymer of N-vinylpyrrolidone and quaternized diethylaminoethyl-methacrylate, having a molecular weight of 10^5 .

To the second class belong as typical examples poly(dimethyldiallyl ammonium chloride) having a molecular weight of 10^5 , and poly(dimethyldiallyl ammonium chloride-acrylamide) having a molecular weight of 2.5×10^5 to 5×10^5 and having a molar percentage ratio of dimethyldiallyl ammonium chloride to acrylamide ranging from

20 : 80 to 80 : 20. To this second class also belongs 1,5-dimethyl-1,5-diazaundecamethylene-polymetho-bromide, having a molecular weight of $5 \cdot 10^3$ - 10^4 .

- 5 To the third class belong 2-hydroxypropyl trimethyl ammonium chloride ethers of hydroxyethyl cellulose, having a molecular weight of 10^5 - 2.5×10^5 .

10 Typical, commercially available polymers belonging to the above classes are Gafquat 734 ex Gaf Corp.; Merquat 550 ex Chemviron, Brussels, Belgium; Polybrene ex Aldrich Chemical Co., Milwaukee, Wisc., USA; Polymer JR 125 and Polymer JR 400 ex Union Carbide, etc.

- 15 The polymers of the invention are used in the machine dishwashing or rinsing composition in an amount of 0.1 to 10%, preferably 0.2 to 1% by weight.

20 The balance of the composition consists of the usual ingredients, present in machine dishwashing or rinsing compositions.

Thus, the machine dishwashing composition usually comprises from 0.1 to 10 % by weight of a nonionic detergent, preferably a low-foaming one. This is a well-known class of nonionic detergents, examples of which are amply described in the textbook "Nonionic Surfactants" by M. Schick. Furthermore, it comprises from 1 to 80% by weight of one or more builder salts, such as alkali metal-ortho-, -pyro-, -tripoly-, -hexametaphosphates, alkali metal citrates, alkali metal carbonates, alkali metal carboxy methyloxysuccinate, alkali metal nitrilo-triacetate, zeolites and so on. In addition, it contains from 1 to 80 % of an alkalinmetal silicate, from 1 to 50 % of an oxygen or chlorine bleaching agent, and it may further contain as optional ingredients perfumes,

germicides, corrosion inhibitors, enzymes, bleach precursors, reducing agents, clays, and so on. Buffer salts, such as borates, can also be included.

5 A rinse composition usually also comprises from 1 to 60%, preferably 10 - 35% by weight of a nonionic detergent, preferably a low-foaming one, and furthermore optional ingredients, such as solvents, (in)organic acids, preservatives, perfumes, dyes, hydrotropes, enzymes, 10 germicides, all in the usual amounts.

It has been found in this respect that it is of specific advantage if the rinsing composition also contains a low level, i.e. 0.1 - 1% by weight of an anionic detergent. 15 The benefits of the present invention are thereby significantly increased in a rinse composition. The anionic detergent can be any well-known type, including fatty acid soaps. Typical examples are alkylaryl sulphonates, alkane sulphonates, olefin sulphonates, 20 alkylsulphates, alkylethersulphates and so on.

Preferred anionic detergents are the alkali metal salts of straight chain C₁₀-C₁₈ alkylbenzene sulphonates, and alkali metal salts of C₁₀-C₁₈ alkylether 25 sulphates, containing from 1 - 10 moles of alkylene oxide. Alkylether carboxylates are also suitable.

The compositions of the present invention can be made in any suitable physical form, such as powders, granulates, 30 tablets, liquids, etc. For machine dishwashing products the granular form is usually prepared, whereas the rinse composition is usually in liquid form. In the latter case, the various ingredients of the rinse composition can naturally also be added to the rinse water.

35 The invention will further be illustrated by way of Example.

Examples A -F

In the following Examples A - F a normal washing procedure was carried out in a commercial domestic dishwashing machine. In the main wash 30 g of a current 5 commercial dishwashing composition was used and at the start of the final rinse cycle 2 ml. of a liquid rinse aid of the following composition were added:

	<u>wt.%</u>
C ₁₂ -C ₁₈ alcohol condensed with ethylene oxide and propylene oxide (Plurafac-RA-30 described in US patent 3 340 309)	10
Citric acid	18
Sodium xylene sulphonate	3
Preservative	0.1
15 Dye	0.006
Water	balance

The tests were carried out with this rinse aid composition as well as with this composition to which either an 20 anionic detergent, a polymer or both were added. The anionic detergent was sodiumdodecylbenzenesulphonate, and the polymer was Gafquat 734, a copolymer of N-vinyl-pyrrolidone and quaternized diethylaminoethylmethacrylate, having a molecular weight of 10⁵.

25 The number of rotations per minute of the lower spray-arm of the dishwashing machine was counted at different temperatures. A decrease in the number indicates a drop in pump pressure; if the number of rotations remains 30 constant, the pump pressure remains constant. The following results were obtained:

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C 800 (R)

Example A

		Number of rotations/min.of lower spray-arm during final rinse					
5	DOBS + Gafquat 734		20°C 25°C 30°C 35°C 40°C 45°C				
	%	%	20	20	23	32	37
	-	-	20	20	23	32	37
	-	2.5	30	30	33	37	39
	0.2	2.5	36	37	38	39	39
10	0.4	2.5	36	38	38	39	40
	0.6	2.5	37	38	39	39	40
	0.8	2.5	36	37	38	39	40

% = % by weight of final composition

15

Example B

		Number of rotations/min.of lower spray-arm during final rinse					
20	DOBS* + Gafquat 734		20°C 25°C 30°C 35°C 40°C 45°C				
	%	%	20	20	23	32	37
	-	-	20	20	23	32	37
	0.1	1.25	32	36	38	38	39
	0.2	2.5	34	36	38	39	40
25	0.3	3.75	34	36	38	39	40
	0.4	5.0	33	36	37	38	39

* DOBS added in acid form

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C 800 (R)

Example C

		Number of rotations/min.of lower spray-arm during final rinse					
5 DOBS + Gafquat 734		20°C	25°C	30°C	35°C	40°C	45°C
%		20	20	23	32	37	39
-	-	20	20	23	32	37	39
0.2	0.85*	32	36	38	39	40	40
0.2	0.85**	35	38	38	39	40	40
10 0.6	2.5 ***	37	38	38	39	40	40
0.6	2.5 **	36	37	38	39	39	39
0.8	3.5 ***	36	37	37	39	40	40
* both mixed first, then added to rinse composition;							
** first Gafquat 734, then DOBS added;							
*** first DOBS, then Gafquat 734 added.							

20

Example D

		Number of rotations/min.of lower spray-arm during final rinse					
25 DOBS + Gafquat 734		20°C	25°C	30°C	35°C	40°C	45°C
%		20	20	23	32	37	39
-	-	20	20	23	32	37	39
0.35	0,85	35	37	38	39	40	40
0.17	0.42	33	36	37	38	38	38
30 0.08	0.21	20	21	24	27	31	33

Example E

		Number of rotations/min.of lower spray-arm during final rinse					
		20°C	25°C	30°C	35°C	40°C	45°C
5	Rinse Aid (R.A.)	20	20	23	32	37	39
	R.A.+2.5% Gafquat 734	30	30	33	37	39	39
	R.A.+2.5% Gafquat 734 + 0.4% DOBS	36	38	38	39	39	40
10	R.A.+2.5% Gafquat 734 + 0.4% LES	36	38	39	39	39	40
	R.A.+2.5% Gafquat 734 + 0.4% SAS	36	37	38	39	39	40
15		LES = Laurylether sulphate (sodium salt)					
		SAS = C ₁₃ -C ₁₇ sec. alkane sulphonate (sodium salt)					

Example F

		Number of rotations/min.of lower spray-arm during final rinse					
		20°C	25°C	30°C	35°C	40°C	45°C
20	R.A. + 0.6% DOBS (acid)	37	38	38	39	40	40
25	2.5% Gafquat 734	36	38	39	39	40	40
	2.5% Merquat 100	36	37	38	39	40	40
	2.5% Merquat 550	36	37	38	39	40	40

Example G

Glass objects were washed in a commercial dishwashing machine using in the main wash 35 g of the following main wash product:

	<u>% by weight</u>
sodium tripolyphosphate	35
sodium metasilicate	49
Plurafac RA 30 (as in Example A)	1
potassium dichlorocyanurate	1.5
water	balance

This was repeated, but then with the same composition to which 0.3 % of Gafquat 734 was added.

15 The appearance of the glass objects with regard to the presence of spots thereon after drying was then assessed according to the following score:

1 = no spots
2 = 1-5 "
3 = 6-10 "
4 = 11-20 "
5 = more than 20 spots.

After one wash, the following results were obtained:

without Gafquat 734: 3.1
25 with " " : 2.3

After four washes:

without Gafquat 734: 4.5
 with " " : 1.0

30 A rinse cycle with a base product according to Examples A - F, compared with this base product to which 10 % Gafquat 734 was added, gave the following results:

one rinse cycle

35 without Gafquat 734: 1.6
with " " : 1.0

four rinse cycles
without Gafquat 734: 2.5
with " " : 1.0

Example H

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A machine dishwashing operation was carried out in a commercial dishwashing machine using the same main wash composition as in Example G at a concentration of 3 g per litre.

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Comparison was made in an identical manner but now using the same main dishwashing composition, to which 0.5% of Gafquat 734 was added.

15

The number of rotations per minute of the lower spray-arm was counted at different temperatures, and the following results were obtained:

Rotational speed of spray-arm

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		<u>without Gafquat 734</u>	<u>with Gafquat 734</u>
	<u>Temperature</u>	20°C	70
		25°C	80
		30°C	88
25		35°C	92
		40°C	95
		50°C	98

C L A I M S

1. A machine dishwashing or rinsing composition comprising a nonionic detergent, characterized in that it contains 0.1 - 10% by weight of polyelectrolytes containing cationic charges and having a cationic charge to carbon atom in the backbone ratio of from 0.03 to 5
5 0.5 and a molecular weight in the range of from $5 \cdot 10^3$ to $5 \cdot 10^5$.
2. A composition according to claim 1, characterized 10 in that the polyelectrolytes further contain neutral or anionic groups, with an anionic to cationic group ratio not greater than 3 : 1.
3. A composition according to claim 1 or 2, characterized 15 in that it contains from 0.2 to 1% by weight of the polyelectrolytes.
4. A composition according to any of the preceding 20 claims, characterized in that the polyelectrolytes are based on quaternized diethylaminoethylmethacrylate, diethyldialkylammonium halide or quaternized polysaccharide.
5. A machine dishwashing composition according to any 25 of the preceding claims, characterized in that it further comprises:
 - (i) 0.1 - 10% by weight of a nonionic detergent,
 - (ii) 1 - 80% by weight of a builder salt,
 - (iii) 1 - 80% by weight of an alkali metalsilicate,
 - 30 (iv) 1 - 50% by weight of a bleaching agent.
6. A rinse composition according to any of the claims 1 - 4, characterized in that it further comprises 1 to 35 60%, preferably 10 to 35% by weight of a nonionic detergent.

7. A rinse composition according to claim 6, characterized in that it further comprises from 0.1 to 1% by weight of an anionic detergent.
- 5 8. A composition according to any of the preceding claims, characterized in that the polyelectrolyte is a copolymer of N-vinylpyrrolidone and quaternized diethylaminoethylmethacrylate.



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EUROPEAN SEARCH REPORT

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Application number

EP 82 20 1271.2

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl. 5)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	<u>EP - A2 - 0 002 085</u> (PROCTER & GAMBLE CO.) * claims 1, 7, 8 * --	1,3,4	C 11 D 3/37 C 11 D 3/22 C 11 D 3/00
A	<u>EP - A1 - 0 013 585</u> (UNILEVER LTD.) * claims 1, 3 ; page 10, paragraph 2 to page 11, paragraph 1 * --		
A	<u>GB - A - 1 527 706</u> (CHEMED CORP.) * claims 1 to 8 * --		TECHNICAL FIELDS SEARCHED (Int.Cl. 5)
A	<u>US - A - 4 203 858</u> (P.M. CHAKRABARTI) * claim 1; column 3, line 58 to column 6, line 2 * --		C 11 D 3/00
A	<u>DE - A1 - 2 717 849</u> (TENNANT CO.) * claims 1, 2 * & <u>FR - A1 - 2 377 447</u> ----		
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons & member of the same patent family. corresponding document
<input checked="" type="checkbox"/> The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
Berlin	29-12-1982	SCHULTZE	